Miscibility and Pressure-Sensitive Adhesive Performances of Acrylic Copolymer and Hydrogenated Rosin Systems

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ABSTRACT: Relationship between the miscibility of pressure-sensitive adhesives (PSAs) acrylic copolymer/hydrogenated rosin systems and their performance (180° peel strength, probe tack, and holding power), which was measured over a wide range of time and temperature, were investigated. The miscible range of the blend system tended to become smaller as the molecular weight of the tackifier increased. In the case of miscible blend systems, the viscoelastic properties (such as the storage modulus and the loss modulus) shifted toward higher temperature or toward lower frequency and, at the same time, the pressure-sensitive adhesive performance shifted toward the lower rate side as the T_g of the blend increased. In the case of acrylic copolymer/hydrogenated rosin acid systems, a somewhat unusual trend was observed in the relationship among the phase diagram, T_g, and the pressure-sensitive adhesive performance. T_g of the blend was higher than that expected from T_gs of the pure components. This trend can be due to the presence of free carboxyl group in the tackifier resin. However, the phase diagram depended on the molecular weight of the tackifier. The pressure-sensitive adhesive performance depended on the viscoelastic properties of the bulk phase. A few systems where a single T_g could be measured, despite the fact that two phases were observed microscopically, were found. The curve of the probe tack of this system shifted toward a lower rate side as the T_g increases. However, both the curve of the peel strength and the holding power of such system did not shift along the rate axis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 651–663, 1999

Key words: acrylic PSA; tackifier; miscibility; phase diagram; peel strength; probe tack; shear creep resistance

INTRODUCTION

Pressure-sensitive adhesive (PSA) is generally a blend of gum and resin. Gum is a linear polymer of very low T_g (-20 to -70°C), and resin is a bulky compound with molecular weight ~ 1000.[1] There are several kinds of PSAs; rubber-based PSA is a blend of rubber and tackifier. Some solvents are used on a process of blending or coating. Hot-melt PSA is a blend of block copolymer and tackifier. No solvent is needed in this type of a blend. In the case of acrylic PSA, it has not been

necessary to involve any tackifier for most applications, because a variety of molecular designs are possible in this category of materials. Recently, there are many cases where tackifiers are blended with acrylic copolymers to modify PSA performance. Other types of PSAs are also blends.

Dealing with blended materials, it is necessary to examine to what extent the components are miscible with each other, because miscibility must have a great influence on phase structure, physical properties, and also practical performance of the materials. Miscibility in natural rubber-based PSAs has been extensively studied by many researchers, such as Hock,[2] Wetzel and Alexander,[3] Sheriff and colleagues,[4] Class and Chu,[5] Kamagata and colleagues,[6] Fukuzawa and Kosaka,[7] and others. Miscibility in hot-melt PSA has been studied by Takashima and Hata,[8] Kraus and Rollmann,[9] Nakajima and colleagues,[10] and many others. However, so far, there have been very few researchers who studied systematically the miscibility in acrylic PSAs or acrylic copolymer/tackifier systems.

We[11–17] have studied the relation between structure/properties of acrylic PSAs and their practical performance. The blends of acrylic copolymer/tackifier are classified into four categories: (1) completely miscible system, (2) lower critical solution temperature (LCST) type system, (3) upper critical solution temperature (UCST) type system, and (4) completely immiscible system. Some of these findings can be qualitatively accounted for on the basis of mean-field approximation.[18] In the case of miscible blend systems, the dynamic mechanical properties of bulk PSA and also the performance of PSA are systematically modified by incorporation of tackifiers. Plots of the PSA performance against the rate (or time) shift along the rate axis (or time axis) as the tackifier content increases. But, in the case of immiscible blend systems, the mechanical properties of the matrix phase in PSA are not modified by incorporation of tackifiers. The PSA performance will mostly depend on the physical properties of the matrix phase, and therefore the plots of the PSA performance against the rate (or time) do not shift along the rate axis (or time axis) in this case. Absolute values of the PSA performance can be modified to some extent because the dispersed phase acts as a kind of filler.[11–18]

Rosin derivatives, which are used for tackifiers in PSAs, are prepared from alcohol and rosin acid. Rosin acid is a mixture of abietic acid and some isomers with the carbon–carbon double bonds in different positions. It is easily oxidized at the position of the carbon–carbon double bonds of rosin acid. This is one of the reason why PSA is deteriorated. So, rosin acids are chemically modified by means of hydrogenation, polymerization, or disproportionation. These modified rosin acids are esterified by some alcohols (methanol, ethanol, diethyleneglycol, glycerol, pentaerythritol, etc.), and the products are used for tackifiers. Comyn[19] studied the chemical characterization of a pentaerythritol rosin ester. However, the PSA performance was not mentioned. In our previous studies,[12–14] the PSA performance was measured as a function of tackifier content in PSA for various systems. However, further studies must be done in terms of the chemical structure of the tackifier systematically.

In this study, miscibility of PSA of acrylic copolymer/hydrogenated rosin systems and their performance (180° peel strength, probe tack, and holding power) are investigated. PSA performance is measured over a wide range of time and temperature, and the relationship among the phase diagram, the mechanical properties of PSA and the PSA performance are clarified.

EXPERIMENTAL

Materials

The acrylic copolymers used in this study are listed in Table I. All of these samples were kindly supplied by Toyo Ink Manufacturing Co., Ltd. (Tokyo, Japan), in the form of the ethyl acetate/toluene solution (84.6/15.4 wt %). Tackifiers were commercially available hydrogenated rosins, which are listed in Table II. These series are esterified by methanol (Hercolyn D), glycerol (Estergum H), or pentaerythritol (Estergum HP), as shown in Table II. Hypale is a nonesterified rosin, and it has a free carboxyl group. They were kindly supplied by Arakawa Chemical Industry Ltd. (Osaka, Japan) and Hercules Inc. (Wilmington, DE). They were all dissolved in ethyl acetate (50/50 vol %), except Hypale. Hypale was dissolved in toluene (50/50 vol %), because it was insoluble in ethyl acetate.

Preparation of the Blends

Acrylic copolymers and tackifiers were blended in ethyl acetate solution in various blend ratios: 90/10, 80/20, and 10/90 (w/w). Solutions were kept at room temperature for 24 days to ensure complete dissolution.

Table I   Acrylic Copolymers[a]

Code	Composition of Copolymers	mol (%)	M_n	M_w	T_g[b] (°C)
No. 1	Butyl acrylate/acrylic acid	(100/0)	79,300	291,600	−36
No. 2	Butyl acrylate/acrylic acid	(97/3)	112,300	417,600	−42
No. 3	Butyl acrylate/acrylic acid	(95/5)	187,600	362,100	−29
No. 4	Butyl acrylate/acrylic acid	(93/7)	154,000	302,500	−23
No. 5	Butyl acrylate/acrylic acid	(90/10)	110,800	241,900	−21
No. 6	Butyl acrylate/acrylic acid	(85/15)	9,600	15,900	−17

[a] Tokyo Ink Manufacturing Co., Ltd.
[b] By differential scanning calorimetry measurements.

Visual Observation

Solution of blends were coated on a slide glass in ~ 40 μm thickness with a glass rod. Solvent in these films on slide glass was allowed to evaporate slowly at room temperature for 24 h, and all the samples were dried at 80°C for 24 h and then dried in a vacuum oven at 110°C for 48 h. After the films on slide glass were maintained at 20°C for 48 h to attain phase equilibrium, they were visually observed to see whether they were transparent (miscible) or opaque (immiscible) at this temperature. Successively, the same procedures were repeated by changing the temperature in a stepwise manner between 50° and 170°C in an air circulation oven.

Microscopic Observation

Blends were coated on the corona-treated poly-(ethylene terephthalate) (PET) film of 25 μm average thickness, using our laboratory coating device. Thickness of the PSA layer was adjusted to 20 μm by a thickness gauge. PSA tapes thus obtained were kept at room temperature in a hood for 24 h to remove most of the solvent very slowly and then dried in an air circulation oven at 80°C for 12 h and 120°C for 12 h. Then, PSA tapes were microscopically observed to see whether we recognize domains (immiscible) or not (miscible) at various temperatures.

Phase Diagram

The phase diagram was determined from the results of visual observation and microscopic observation.

Preparation of PSA Tape

Dried PSA tapes were obtained as described in the section on "Microscopic Observation." PSA tapes were pressed onto release coating paper by a 2-kg rubber roller. Then they were conditioned at 20°C and 65% relative humidity for more than 14 days. Thus, PSA specimens for performance tests were prepared.

Table II   Tackifier Resins

Resin Type	Commercial Name	Alcohol Type	S.P.[a] (°C)	T_g[b] (°C)	A.V.[c]	M_n[d]	M_w[d]
Hydrogenated rosin	Hercolyn D[e]	Methanol	liquid	−27 (−34)[f]	4–8	232	244
	Estergum H[g]	Glycerol	72	38	6.1	673	853
	Estergum HP[g]	Pentaerythritol	92	51	18.4	683	1018
	Hypale[g]	—	72	38	162.8	280	304

[a] S.P. = softening point, in the literature.
[b] By differential scanning calorimetry measurements.
[c] A.V. = acid value, in the literature.
[d] By gel permeation chromatography (Arakawa Chemical Industries, Ltd.).
[e] Hercules, Inc.
[f] In the literature.
[g] Arakawa Chemical Industries, Ltd.

Measurement of PSA Performance

A blend ratio (acrylic copolymer/tackifier) was fixed to 8/2 in this study, because the purpose of this study is to compare the characteristics of the PSA performance in terms of the chemical structure of the tackifier.

We measured the PSA performance as a function of temperature and rate of separation. In most of the testing standards, PSA performance is measured at a fixed rate of separation, fixed stress (σ_0), and fixed temperature. However, we have to consider that the PSA performance is quite rheological, and we measured the PSA performance over a wide range of rate, stress, and temperature.

Measurement of 180° Peel Strength

Peel strength was a measure of a force required to remove a PSA film from an adhered one. In this study, an aluminum plate was used as an adherend. The aluminum adherend was cleaned with acetone and then with trichloroethylene beforehand. The PSA tape was pressed on the aluminum adherend by a 2 kg rubber roller passing over two times. The 180° peel strength P was measured as a function of the peeling rate in a range from 10^{-4} to 10^1 cm s^{-1} at 20°C by using a driving part of the rolling friction tester based on the pulling cylinder method.[20] Specimens were kept at 20°C for 24 h. Test results were an average of five measurements under the same conditions.

Measurement of Probe Tack

Probe tack provided a measure of a tackiness of a PSA ability to wet-out a surface instantaneously. A test was conducted on the Polyken Probe Tack Tester [Tokyo Seiki Seisaku-sho, Ltd. (Tokyo, Japan)] with a polished stainless-steel probe 5 mm in diameter, which was designed to measure a maximum force (peak) required to break an adhesive bond (gf cm^{-2}) when the probe is placed in contact with a flat film at controlled rates of separation, temperatures, contact pressure, and dwell time. Measurements were conducted at six different temperatures (13, 23, 33, 43, 50, and 60°C), and at nine different rates of separation (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 cm s^{-1}) under a constant pressure of 100 gf cm^{-2} and a dwell time of 1 sec. Test results were an average of seven measurements under the same conditions. And the master curves are obtained by applying the time (rate)-temperature superposition principle.

Measurement of Shear Creep Resistance (Holding Power)

Holding time (t_b) was a measure of the ability of PSA to withstand pressure from another adherend under constant stress (σ_0) at a certain temperature. σ_0 pulled the PSA tape downward from a vertically placed test adherend in a direction parallel to the surface of bonding. In this study, an aluminum plate was used as an adherend. The aluminum adherend was cleaned with acetone and then with trichloroethylene beforehand. PSA tapes were pressed onto the aluminum adherend by a 2 kg rubber roller passing over them twice. Test samples were prepared to form a bonding area of 1 inch × 1 inch. Also, they were loaded at various levels of stress (σ_0) and at fixed temperature. The time to slip completely (the holding time, t_b) was recorded as the failure time by model CP6-L-500 of Orientec Co. (Tokyo, Japan). Test results were an average of three measurements under the same conditions.

T_g Measurement

A purpose of this study is to investigate the relation among the miscibility of PSA, the mechanical properties of PSA, and PSA performance. In this study, a blend ratio (acrylic copolymer/tackifier) was fixed to 8/2. T_gs of both tackifiers and blends were measured with a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating rate of 40°C min^{-1} in a helium purge. In all cases, T_g was taken as the midpoint of the heat capacity curve change with temperature and obtained from the second scanning.

RESULTS AND DISCUSSION

Characterization of Tackifier Resins

Characterizations of tackifiers are listed in Table II. The alcohol component of the tackifier is bulkier, the softening point, the T_g, the acid value, and the molecular weight tend to increase. Table III shows both a series of the T_gs of the tackifiers and a series of the T_gs of the blends of acrylic copolymer/tackifiers. The T_gs of the blends are elevated, as the molecular weight of the tackifier is increases. In case of Hypale, a somewhat exceptional trend was observed. Hypale is a nonesterified rosin, and it has the smallest bulkiness in this study. However, both the softening point and the T_g of Hypale are equal to those of Estergum H. T_gs of acrylic copolymer/Hypale are higher

Table III $T_g{}^a$ of the Blend of the Acrylic Copolymer/Tackifier (8/2) System

Resin Type	Commercial Name	Alcohol Type	Tackifier Only (°C)	Acrylic Copolymer No. 2 (°C)	Acrylic Copolymer No. 5 (°C)
Hydrogenated rosins					
	Polymer only	—	—	−42	−21
	Hercolyn D[b]	Methanol	−27	−47	−33
	Estergum H[c]	Glycerol	38	−35	−14
	Estergum HP[c]	Pentaerythritol	51	−28	−7
	Hypale[c]	—	38	−28	−12

[a] By differential scanning calorimetry measurements.
[b] Hercules, Inc.
[c] Arakawa Chemical Industries Ltd.

than those of acrylic copolymer/Estergum H. Because Hypale has a free carboxyl group, it can form an intramolecular or an intermolecular hydrogen bond, which is the reason why the T_gs of the Hypale-containing systems are extraordinarily elevated.

Phase Diagram

Phase diagrams of acrylic copolymer/Hercolyn D are shown in Figure 1(a). The components of these systems are completely miscible, irrespective of the acrylic acid content in the copolymers.

Phase diagrams of acrylic copolymer/Estergum H are shown in Figure 1(b). Blends of acrylic homopolymer No. 1/Estergum H give the phase diagram with both LCST, a type whose critical temperature (T_c) is 150°C, and whose UCST type is 120°C. When the content of the acrylic acid in the copolymer is 3%, the phase diagram converted to UCST whose T_c is 120°C. As the content of the acrylic acid increases further, a miscible zone in the phase diagram of the blends decreases.

Phase diagrams of acrylic copolymer/Estergum HP are shown in Figure 1(c). The blends of acrylic homopolymer No. 1/Estergum HP give the phase diagram of a typical LCST, whose T_c is 140°C. When the content of the acrylic acid in the copolymer is 3 to 7%, the blends are miscible at any temperature between 20° and 170°C, irrespective of the tackifier content. It is interesting to note that, at above 10% of the acrylic acid content, the phase diagram changes to the UCST type. Acrylic copolymer (acrylic acid content 7%) is completely miscible with Estergum HP, which means that T_c of this system is lower than room temperature. Phase diagram of the blend of acrylic copolymer (acrylic acid content: 15%) and the same resin is of the UCST type with T_c higher than 170°C.

These facts make us believe that the blend of acrylic copolymer (acrylic acid content 10%) and Estergum HP has a phase diagram of UCST type. An immiscible zone in the phase diagram increases as the acrylic acid content in the copolymer increases further.

It was found previously[16–18] that the miscibility between acrylic copolymer and rosin (esters of rosin) and also that between the same series of copolymer and superesters (esters of disproportionated rosin) tends to be poorer as the alcohol part of the ester becomes bulkier. In this study, pentaerythritol ester (Estergum HP) and glycerol ester (Estergum H) of rosin, the former being bulkier, were used, but the immiscible zone in the phase diagram of Estergum HP system is smaller than that in the Estergum H system, which is not in agreement with the previously described empirical correlation between miscibility and bulkiness of the tackifier. However, we have to note the fact that both tackifier resins have a broad distribution of molecular weight. Gel permeation chromatography chromatograms show that Estergum HP contains much more low molecular weight components than Estergum H does, and the phase diagrams must have been modified by these components. But, on average, the miscible range of a blend system is smaller as the molecular weight of a tackifier increases. The term "bulkiness," which appeared in previous reports,[16–18] can be replaced by "molecular weight of the tackifier," "molar volume of the tackifier," or "the number of the hydroxyl group in the alcohol component of the tackifier: monol, diol, triol, tetrol, etc. etc."

Another example is shown in Figure 1(d), where a miscible zone in the phase diagram of the acrylic copolymer/Hypale system is not smaller

(a)

Figure 1 (a) Phase diagrams of acrylic copolymer and Hercolyn D systems. (b) Phase diagrams of acrylic copolymer and Estergum H systems. (c) Phase diagrams of acrylic copolymer and Estergum HP systems. (d) Phase diagrams of acrylic copolymer and Hypale systems. (○) Transparent (miscible), (●) opaque (immiscible), and (◎) intermediate. AA = acrylic acid.

than that of the acrylic copolymer/Hercolyn D system, despite the fact that bulkiness of Hypale is smaller than that of Hercolyn D. The molecular weight of Hypale is larger than that of Hercolyn D, which is esterified by methanol. This might be due to the presence of the free carboxyl group, which Hypale has and Hercolyn D does not have.

(b)

Figure 1 (*Continued from the previous page*)

PSA Performance of Acrylic Copolymer No. 2 (Butyl Acrylate/Acrylic Acid-97/3) and Tackifier Systems

All of the blends of acrylic copolymer no. 2/tackifiers (8/2) are miscible in the temperature range of performance tests in this experiment.

The peel strength P plotted against logarithm of the rate of separation is shown in Figure 2, where a curve has a peak at some rate. As the T_g of the blend becomes higher, the peak shifts toward the lower rate side. The cohesive failure occurs in lower rate region of the curve, and the slip-stick failure occurs around the peak. The interfacial failure (adherend/PSA) occurs in a higher rate region of the curve. Another peak tends to appear when the rate increases further than 10^1 cm s^{-1}, and the interfacial failure [PSA/

Figure 1 (*Continued from the previous page*)

substrate (PET)] occurs around this second peak. The T_gs of both Estergum H and Estergum HP are so high that the interfacial failure (PSA/substrate) is clearly observed. These results show that the PSA performance depends on the viscoelastic properties of the bulk phase of the PSA systems, and they are modified by blending base polymer with the miscible tackifiers. Although the T_g of Hypale is equal to that of Estergum H, T_g of the acrylic copolymer No. 2/Hypale system is higher than that of the acrylic copolymer No. 2/Estergum H system. This can be because Hypale has a free carboxyl group, which might cause some degree of hydrogen bonding between copolymer and tackifier, and the T_g of the blend is higher than that expected from T_gs of the pure

(d)

Figure 1 (*Continued from the previous page*)

components. It is ascertained again that PSA performance depends on the viscoelastic properties (or the T_g) of the bulk phase of the PSA systems.

The probe tack is measured as a function of both the temperature and the rate of separation, and the master curves are obtained by applying the rate temperature superposition principle to the data. The master curves of probe tack are shown in Figure 3. The mastercurve of the probe tack shifts along the rate axis toward the lower rate side as the T_g of the blend increases. The probe tack of acrylic PSA has been studied systematically by Zosel.[21] He pointed out that the probe tack energy becomes maximum at some temperature that is close to the T_g of PSA, and

Figure 2 Plots of peel strength against the logarithm of rate of separation for acrylic copolymer (No. 2) and tackifier systems. C = Cohesive failure, SS = slip-stick failure, I-1 = interfacial failure (adherend/PSA), I-2 = interfacial failure (PSA/substrate).

that a peak height increases as G_{en}, or the entanglement modulus of PSA decreases. Experimental data of this study are substantially in agreement with Zosel's findings. The blend of acrylic copolymer No. 2/Hypale system shows somewhat special performance of the probe tack, just as described in the peel strength.

The holding power or the shear creep resistance, which is measured as the time to break (t_b), depends on the stress (σ_0). As Figure 4

Figure 3 Master curves of probe tack for acrylic copolymer (No. 2) and tackifier systems. (○) 13°C, (●) 23°C, (□) 33°C, and (■) 43°C.

Figure 4 Plots of σ_0 against logarithm of t_b for acrylic copolymer (No. 2) and tackifier systems. (●) Acrylic copolymer (butyl acrylate/acrylic acid = 97/3), (○) acrylic copolymer/Hercolyn D (8/2), (■) acrylic copolymer/Estergum H (8/2), (□) acrylic copolymer/Hercolyn HP (8/2), and (▲) acrylic copolymer/Hypale (8/2).

shows, the plots of σ_0 against a logarithm of t_b give monotonically decreasing curves. As the T_g of the blend increases, the viscoelastic properties such as the storage modulus and the loss modulus shift toward higher temperature or toward the lower frequency side, and the curves in Figure 4 shift toward a longer time region. Again, we found somewhat special correlation between the viscoelastic properties or T_g and the shear creep resistance for the blend of acrylic copolymer No. 2/Hypale system.

PSA Performance of Acrylic Copolymer No. 5 (Butyl Acrylate/Acrylic Acid-90/10) and Tackifier Systems

The blends of acrylic copolymer No. 5/tackifiers (8/2) are miscible in the temperature range of performance tests in this experiment, except the blend of acrylic copolymer No. 5/Estergum H.

The plots of P versus logarithm of the rate are shown in Figure 5. A curve for acrylic copolymer No. 5 without tackifier has a peak at the rate between 10^{-2} and 10^{-1} cm s^{-1}. The cohesive failure occurs in a lower rate region of the curve, and the interfacial failure (adherend/PSA) occurs in higher rate region of the curve. In the case of miscible blend systems (Hercolyn D, Estergum HP, and Hypale), the cohesive failure does not

Figure 5 Plots of peel strength against the logarithm of rate of separation for acrylic copolymer (No. 5) and tackifier systems. C = Cohesive failure, SS = slip-stick failure, I-1 = interfacial failure (adherend/PSA), and I-2 = interfacial failure (PSA/substrate).

occur within the range of the peeling rate in this experiment. To make sure of a change of the failure mode, the peel strength of the blend of acrylic copolymer No. 5/Hercolyn D system was measured at 35°C, and the cohesive failure was observed at a rate of 10^{-3} cm s^{-1}. This result shows that the curve of the blend of acrylic copolymer No. 5/Hercolyn D system may have a peak at some rate in a lower rate region than shown in Figure 5. This peak may correspond to the peak at 10^{-2} cm s^{-1} found in case of acrylic copolymer No. 5 without tackifier. This result is similar to that of the acrylic copolymer No. 5/Estergum HP system. In case of the acrylic copolymer No. 5/Hypale system, the failure mode was observed at 35°, 50°, 80°, 100°, and 120°C when the peel test was performed at a constant rate of 10^{-4} cm s^{-1}; and, in every case, only the interfacial failure (adherend/PSA) was observed. From this result, it is suggested that the interfacial failure (adherend/PSA) may occur at 20°C in the rate region lower than 10^{-4} cm s^{-1}. This may be due to the fact that Hypale has a free carboxyl group, and cohesive energy of the blend of acrylic copolymer/nonesterified tackifier (Hypale) may be higher than that of the acrylic copolymer/esterified tackifier. In case of an immiscible blend system (acrylic copolymer No. 5/Estergum H), plots of P versus logarithm of the rate have two peaks at some rates. The cohesive failure occurs at a region of the rate lower than the lower rate peak, and in-

terfacial failure (adherend/PSA) appears at rates between a region of the two peaks. The interfacial failure [PSA/substrate (PET)] occurs at a region of the rate higher than the higher rate peak. It is suggested that, in case of immiscible blend systems, the curve of P shifts toward the lower rate region to a much lesser extent than that in cases of miscible blend systems.

The probe tack is measured as a function of both the temperature and rate of separation, and master curves are obtained by applying the rate-temperature superposition principle to the data. Master curves of the probe tack are shown in Figure 6. They shift along the rate axis toward the lower rate side as the T_g of the blend increases. This is substantially in agreement with Zosel's findings mentioned previously. It is interesting to note again that bulkiness of Hypale is the smallest, but the curve of the probe tack of acrylic copolymer No. 5/Hypale shifts toward the lower rate side to a great extent. It is evident that PSA performance depends on the viscoelastic properties of the bulk phase of the PSA system. In case of acrylic copolymer No. 5/Estergum H, a single T_g could be measured despite the fact that two phases were observed microscopically. PSA performance of this system shifted toward the lower rate side as the T_g increases just as in the case of miscible blend systems. The acrylic copolymer No. 5 and Estergum H are miscible with each other within the concentration of 20–30%, within which the T_g of the matrix phase increases. But, in the range where the phase separation occurs, the T_g of the matrix phase is almost constant. In a strict sense, the tackifier consists of many com-

Figure 6 Master curves of probe tack for acrylic copolymer (No. 5) and tackifier systems. (○) 13°C, (●) 23°C, (□) 33°C, (■) 43°C, (◇) 50°C, (◆) 60°C.

Figure 7 Plots of σ_0 against logarithm of t_b for acrylic copolymer (No. 5) and tackifier systems. ($\bigcirc$, $\square$, and $\blacktriangle$) Interfacial failure (PSA/adherend), ($\bullet$) acrylic copolymer (butyl acrylate/acrylic acid = 90/10), ($\bigcirc$) acrylic copolymer/Hercolyn D (8/2), ($\blacksquare$) acrylic copolymer/Estergum H (8/2), ($\square$) acrylic copolymer/Estergum HP (8/2), and ($\blacktriangle$) acrylic copolymer/Hypale (8/2).

ponents. So, if lower molecular weight components of the tackifier are soluble in the matrix phase, the T_g of the matrix phase can increase to some extent. If the amount of the resin-rich phase is much smaller than that of the matrix phase, the T_g of the resin-rich phase may not be observed. At all events, the probe tack performance is influenced by the viscoelastic properties of the matrix phase. The probe tack performance shifts toward the lower rate side as the T_g of the matrix phase is elevated. This phenomenon is in contrast to the case of the peel strength. Namely, in case of acrylic copolymer No. 5/Estergum H system, the peel strength depends on the physical properties of the matrix phase, and the tackifier acts as a kind of filler. So, the curve of the peel strength does not shift along the rate axis just like a typical immiscible blend system.

The holding power or the shear creep resistance of acrylic copolymer No. 5/tackifier systems are shown in Figure 7. The plots of σ_0 against the logarithm of t_b give monotonically decreasing curves. In case of miscible blend systems (Hercolyn D, Estergum HP, and Hypale), the curve shifts toward a longer time scale as the T_g of the tackifier (or the blend) is elevated. It is noteworthy that, in the case of the acrylic copolymer No. 5/Hercolyn D system, the degree of the shift is greater than that of the acrylic copolymer No.

5/Estergum HP system, whereas the molecular weight of Hercolyn D is not larger than that of Estergum HP. The interfacial failure (adherend/PSA) was observed in this system (Hercolyn D). In the case of the immiscible blend system (acrylic copolymer No. 5/Estergum H), the curve does not change greatly even if the tackifier is added. In this system, the T_g of the blend increases to some extent as the tackifier is added, despite the fact that two phases are observed microscopically. It is believed that the holding power of PSA are dependent on the rubbery plateau modulus (G'_{en}).[22] If G'_{en} of PSA does not increase, no matter how the T_g of PSA may be, the curve of the holding power does not shift along the time scale.

CONCLUSIONS

1. Hydrogenated rosin esters are characterized. The softening point—the T_g, the acid value, and the molecular weight tend to increase as an alcohol, which is the component of the tackifier resin—becomes bulkier. The T_g of the blend of acrylic copolymer/hydrogenated rosin ester systems also tends to increase as the molecular weight of the tackifier increases.
2. Miscibility of the acrylic copolymer and the tackifier tends to become poorer as the molecular weight or the tackifier increases.
3. In the case of miscible blend systems, as the molecular weight of the tackifier increases, the viscoelastic properties (such as the storage modulus and the loss modulus) shift toward a higher temperature or toward lower frequency. At the same time, the curves of both peel strength and probe tack shift toward the lower rate side, and the curve of the shear stress σ_0 plotted against the logarithm of t_b shifts toward a longer time scale along the t_b axis.
4. The T_g of acrylic copolymer/hydrogenated rosin acid system was higher than that expected from the T_gs of the pure components, which can be due to the presence of a free carboxyl group in the nonesterified rosin acid. However, the phase diagram depended on the molecular weight of the tackifier. PSA performance depended on the viscoelastic properties of the bulk phase.
5. A few systems were found where a single T_g could be observed, although we recognized two phases microscopically. The curve of the probe tack of these systems

shifts toward the lower rate side as the T_g is elevated, just as the ordinary miscible systems do. However, both the curves of peel strength and the holding power of such systems did not shift much along the rate axis, just as the immiscible systems do not.

6. To investigate PSA performance, it is important to measure PSA performance over a wide range of time and temperature. Both phase diagram and viscoelastic properties of the PSA are important factors.

REFERENCES

1. Schlademan, J. A. in Handbook of Pressure-Sensitive Adhesive Technology, 2nd ed., D. Satas, Ed., Van Nostrand Reinhold, New York, 1989.
2. Hock, C. W. Adhesives Age 1964, March, 21.
3. Wetzel, F. H.; Alexander, B. B. Adhesives Age 1964, January, 28.
4. Sheriff, M.; Knibbs, R. W.; Langley, P. G. J Appl Polym Sci 1973, 17, 3423.
5. Class, J. B.; Chu, S. G. J Appl Polym Sci 1985, 30, 805.
6. Kamagata, K.; Kosaka, H.; Hino, K.; Toyama, M. J Appl Polym Sci 1971, 15, 483.
7. Fukuzawa, K.; Kosaka, T. Preprints of 6th Symposium on Adhesion and Adhesives, Tokyo, Japan, 1968, p. 51.
8. Takashima, Y.; Hata, T. J Adhesion Soc Jpn 1978, 14, 245.
9. Kraus, G.; Rollmann, K. W. J Appl Polym Sci 1977, 21, 3311.
10. Nakajima, N.; Babrowicz, R.; Harrell, E. R. J Appl Polym Sci 1992, 44, 1437.
11. Naruse, S.; Kim, H.-J.; Tsukatani, T.; Kajiyama, M.; Takemura, A.; Mizumachi, H.; Hatano, Y. J Adhesion 1994, 47, 165.
12. Kim, H.-J.; Mizumachi, H. J Appl Polym Sci 1995, 56, 201.
13. Kim, H.-J.; Mizumachi, H. J Appl Polym Sci 1995, 58, 1891.
14. Kim, H.-J.; Mizumachi, H. J Adhesion 1995, 49, 113.
15. Hayashi, S.; Kim, H.-J.; Mizumachi, H. J Adhesion Soc Jpn 1995, 31, 407.
16. Hayashi, S.; Kim, H.-J.; Kajiyama, M.; Ono, H.; Mizumachi, H.; Zufu, Z. J Adhesion Soc Jpn 1997, 33, 258.
17. Hayashi, S.; Kim, H.-J.; Kajiyama, M.; Ono, H.; Mizumachi, H.; Zufu, Z. J Pack Sci Technol Jpn 1997, 6, 191.
18. Kim, H.-J.; Mizumachi, H. J Appl Polym Sci 1995, 57, 175.
19. Comyn, J. Int J Adhesion Adhesives 1995, 15, 9.
20. Mizumachi, H. J Appl Polym Sci 1985, 30, 2675.
21. Zosel, A. Adhesives Age 1989, October, 42.
22. Hata, T.; Tsukatani, T.; Mizumachi, H. J Adhesion Soc Jpn 1994, 30, 311.